

Interaction of copernicium with gold: Assessment of applicability of simple density functional theories

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Interactions of Cn (element 112) atoms with small Au clusters are studied using accurate *ab initio* scalar relativistic coupled cluster method for correlation treatment and two-component relativistic density functional theory (RDFT) to account for spin-dependent relativistic effect. The results demonstrate the failure of RDFT with simple generalized-gradient and hybrid functionals in describing Cn–Au bonds in complex systems.

Successful identification of superheavy element 112 (Cn) by thermochromatography on gold surface [1, 2] had resulted in an avalanche of theoretical studies of the nature and properties of the interactions of the Cn atom with gold (see [3–5] and references therein). It is generally believed (see, e.g., [4]) that the relativistic density functional theory (RDFT) with simple generalized gradient approximations (GGA) for the exchange-correlation functional (XCF) [6, 7] provides a satisfactory tool for theoretical modeling of Cn/Au surface complexes. Since the quantitative experimental information on Cn–Au interactions is restricted to a single measured value, the adsorption temperature of Cn on gold surface, thus being obviously insufficient to estimate the reliability of theoretical approaches, the main argumentation for the validity of RDFT/GGA in applications to their description relies on the data concerning diatomic systems (see e.g. [8]) and on the experience of calculations of other heavy element compounds. It should be noticed, however, that the bulk of such experience is nearly useless because of unique features of the Cn atomic structure in the valence region. The presence of relatively compact filled *d*-shell with rather high orbital energies (resembling that in Au and Hg) enables one to expect unusually strong $d_{\text{Cn}}^{10} - d_{\text{Au}}^{10}$ contributions to the Cn–Au bonding, in a sense similar to the aurophilic attraction [9]. The efficiency of the RDFT with semilocal functionals in such cases is at least questionable as demonstrates the example of the Au_n cohesion energy which is nicely reproduced by RDFT/GGA in the Au diatomic but becomes progressively underestimated for larger clusters and bulk [10, 11]. The dependence of the accuracy of RDFT/GGA based results for gold clusters on the coordination numbers of Au atoms has been shown in Ref. [10].

The mentioned facts inspire serious doubts concerning the adequacy of the RDFT/GGA treatment of the systems under discussions. These doubts are strengthened by the detailed pilot comparison of the results of relativistic DFT and many-body perturbation theory (MBPT) calculations on moderate-size Hg– Au_n and Cn– Au_n complexes [5]. Unfortunately, finite-order MBPT binding energies for similar (Au- and Hg-containing) systems are

strongly affected by convergency problems and the re-summation scheme chosen in this work was not optimal [12]. The errors due to the use of rather restricted one-electron basis sets with insufficient flexibility of high angular momentum components can also be non-negligible. A more accurate correlation treatment is, therefore, required to pronounce the decisive verdict.

In the present Letter we report the calculations on Cn– Au_n complexes, $n = 1-4$, by a hybrid scheme combining *ab initio* scalar relativistic correlation calculations with the estimation of spin-dependent relativistic effects (effective spin-orbit couplings) through geometry-dependent corrections to interaction energies (Δ_{SO}) obtained at the RDFT level [8]. The necessary accuracy of the correlation treatment is ensured by the use of an accurate coupled cluster technique and the extrapolation to the complete basis set limit. We have to stress that our scheme does not imply the smallness of spin-dependent interactions or the neglect of their interference with electron correlations [13]. The geometries of polyatomic systems ($n = 2-4$) were restricted to those resembling possible structures of adsorption complexes on the gold (111) surface, namely, the C_{2v} configurations of Cn– Au_2 and Cn– Au_4 , as well as the C_{3v} configuration of Cn– Au_3 simulating the “bridge” and “hollow” positions of the Cn adatom, respectively. The Au–Au distances were fixed at their bulk value (2.884 Å); only the distances r between the Cn atom and the center of the Au subsystem were optimized.

The computational scheme employed in the present study resembles that used in Ref. [14]. The “small” atomic cores (60 electrons for Au and 92 electron for Cn) were replaced by accurate shape-consistent semilocal relativistic pseudopotentials (RPPs) [15, 16] optimized for the description of valence shells. Scalar relativistic calculations were performed with the spin-averaged version of these RPPs by the conventional coupled cluster method with fully optimized single and double and perturbative triple amplitudes, CCSD(T), implemented in the CFOUR program package [17]. For the systems with odd numbers of gold atoms unrestricted Hartree–Fock references were used. The innermost explicitly treated atomic shells

(6s6p for Cn and 5s5p for Au) were not correlated.

We used the correlation-consistent basis sets ([14, 18]) constructed according to the prescriptions from Ref. [19]. Taking into account the experience of calculations on Au-Au and Au-Hg [12, 19], the bases were augmented by diffuse functions (the “aug-cc” variant). The complete basis set limit (CBS) estimates were derived from the energies obtained with triple and quadruple zeta quality bases using the conventional two-point formula [20]. As has been pointed out in Ref. [14], the extrapolation procedure efficiently suppresses basis set superposition errors, so that we had no need to invoke any counterpoise procedure.

The contributions from the spin-dependent relativistic effects to the interaction energies were evaluated by comparing the results of one- and two-component (1c and 2c) non-collinear RDFT calculations performed with the code [21]. The data presented in this letter were obtained with simple generalized gradient approximation [6, 7] usually denoted by the acronym B88P86 and believed to be well suited for superheavy element electronic structure calculations, and with PBE0 hybrid functional [22] chosen because of its (partially) non-empirical nature.

The main results of the calculations are listed in Table I. The equilibrium separations and binding energies derived from 1c CCSD(T)/CBS+ Δ_{SO} potential curves for the CnAu diatomic molecule are in very reasonable agreement with those obtained by RDFT with both XCFs employed. When the cluster size increases, the 2c RDFT binding energies deviate *progressively* from their 1c CCSD(T)+ Δ_{SO} counterparts; for the largest system under study the underestimation of the binding energy reaches ca. 40-45 %. It might be interesting to notice that the results of a similar numerical experiment with Cn replaced by the neighbor element 113 (E113) with markedly lower energies of the filled *d* shell do not exhibit a similar trend.

The extrapolated MBPT+ Δ_{SO} binding energies for Cn–Au₄ from Ref. [5] are visibly too large; nevertheless, the main conclusion of the cited work concerning the failure of RDFT with simple GGA and GGA-based hybrid energy functionals in describing more or less complex Cn–Au systems is confirmed by the present accurate calculations. A reasonable agreement between the most recent RDFT/GGA Cn/Au adsorption energy estimate (0.46 eV, [3]) and the presently assumed experiment-based value (0.54^{+4}_{-3} eV, [2]) seems not to be sufficient to prove the opposite opinion and, probably, results from a fortuitous cancellation of errors in [3] (for instance, those of approximate nature of the B88P86 functional and of use of purely local functional to get the electron and magnetization density distributions).

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TABLE I: Equilibrium *r* values (Å) and Cn-Au_{*n*} binding energies (eV).

	CnAu	CnAu ₂	CnAu ₃	CnAu ₄
<i>r_e</i> , 2c RDFT/B88P86	2.73	2.65	2.61	2.68
2c RDFT/PBE0	2.74	2.72	2.63	2.68
1c CCSD(T)+ Δ_{SO}^{B88P86}	2.73	2.63	2.59	2.64
1c CCSD(T)+ Δ_{SO}^{PBE0}	2.72	2.65	2.60	2.67
MBPT+ Δ_{SO}^{B88P86} *)	2.78			2.60
MBPT+ Δ_{SO}^{PBE0} *)	2.77			2.61
<i>D_e</i> , 2c RDFT/B88P86	0.47	0.23	0.29	0.25
2c RDFT/PBE0	0.39	0.19	0.28	0.26
1c CCSD(T)+ Δ_{SO}^{B88P86}	0.45	0.33	0.45	0.46
1c CCSD(T)+ Δ_{SO}^{PBE0}	0.42	0.29	0.42	0.42
1c MBPT+ Δ_{SO}^{B88P86} *)	0.37			0.60
1c MBPT+ Δ_{SO}^{PBE0} *)	0.35			0.55

*) Ref. [5]; fourth-order MBPT was followed by the extrapolation using constrained [3/2] Padé approximant.

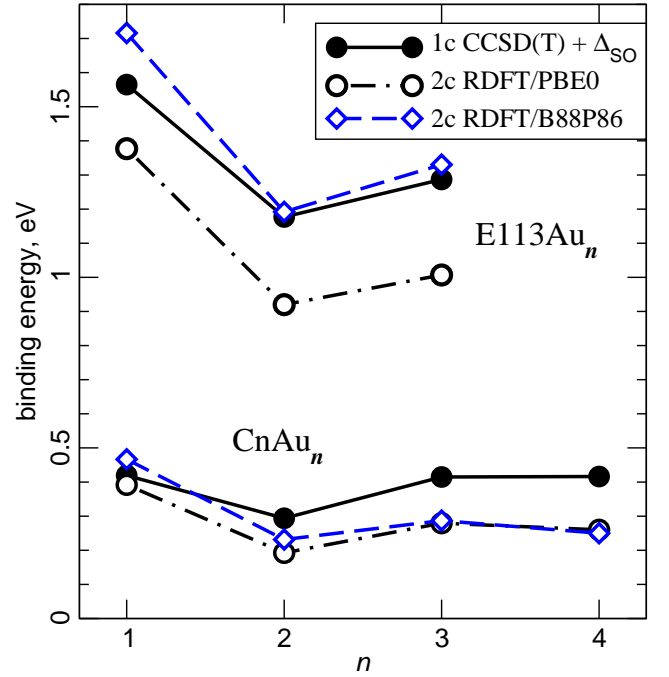


FIG. 1: The dependencies of CCSD(T)+ Δ_{SO} and RDFT binding energies on gold cluster size. The data on E113–Au_{*n*} systems are taken from Ref. [14].

- [1] R. Eichler, N.V. Aksenov, A.V. Belozarov, G.A. Bozhikov, V.I. Chepigin, S.N. Dmitriev, R. Dressler, H.W. Gäggeler, V.A. Gorshkov, F. Haenssler, M.G. Itkis, A. Laube, V.Ya. Lebedev, O.N. Malyshev, Yu.Ts.

- Oganessian, O.V. Petrushkin, D. Piguet, P. Rasmussen, S.V. Shishkin, A.V. Shutov, A.I. Svirikhin, E.E. Tereshatov, G.K. Vostokin, M. Wegrzecki, and A.V. Yeremin, *Nature* 447, 72–75 (2007)
- [2] R. Eichler, N.V. Aksenov, A.V. Belozero, G.A. Bozhikov, V.I. Chepigin, S.N. Dmitriev, R. Dressler, H.W. Gäggeler, A.V. Gorshkov, M.G. Itkis, F. Haenssler, A. Laube, V.Ya. Lebedev, O.N. Malyshev, Yu.Ts. Oganessian, O.V. Petrushkin, D. Piguet, A.G. Popeko, P.Rasmussen, S.V. Shishkin, A.A. Serov, A.V. Shutov, A.I. Svirikhin, E.E. Tereshatov, G.K. Vostokin, M. Wegrzecki, and A.V. Yeremin, *Angew. Chem. Int. Ed.* 47 (2008) 3262–3266
- [3] V. Pershina, J. Anton, and T. Jacob, *J. Chem. Phys.* 131 (2009) 084713
- [4] V. Pershina, *Radiochim. Acta* 99 (2011) 459–476
- [5] A. Zaitsevskii, C. van Wüllen, and A.V. Titov, *J. Chem. Phys.*, 132 (2010) 081102
- [6] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098–3100
- [7] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822–8824
- [8] A. Zaitsevskii, E. Rykova, N.S. Mosyagin, and A.V. Titov, *Cent. Eur. J. Phys.* 4, No.4, 448–460 (2006)
- [9] S.G. Wang, W.H.E. Schwarz, *J. Am. Chem. Soc.* 126 (2004) 1266–1276
- [10] A.A. Rusakov, E. Rykova, G.E. Scuseria, and A. Zaitsevskii, *J. Chem. Phys.* 127 (2007) 164322
- [11] O.D. Häberlen, S.-Ch. Chung, M. Stener, and N. Rösch, *J. Chem. Phys.* 106, (1997) 5189
- [12] A. Zaitsevskii, *Chem. Phys. Lett.* 495 (2010) 141–145
- [13] A.V. Zaitsevskii, E.A. Rykova, and A.V. Titov, *Russian Chem. Rev.* 77 (2008) 205–218
- [14] A. Zaitsevskii, A.V. Titov, A.A. Rusakov, and C. van Wüllen, *Chem. Phys. Lett.*, 508 (2011) 329–331
- [15] N.S. Mosyagin, A.N. Petrov, A.V. Titov, and I.I. Tupitsyn, *Progr. Theor. Chem. Phys.*, B 15 (2006) 229–251
- [16] N.S. Mosyagin, A. Zaitsevskii, and A.V. Titov, *Int. Rev. At. Mol. Phys.* 1 (2010) 63–72
- [17] CFOUR, a quantum chemical program package written by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W.J. Lauderdale, D.A. Matthews, T. Metzroth, D.P. O’Neill, D.R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen (2010)
- [18] Basis set parameters can be found at <http://www.qchem.pnpi.spb.ru/recp>
- [19] K.A. Peterson and C. Puzzarini, *Theor. Chem. Acc.* 114 (2005) 283–296
- [20] T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* 106 (1997) 9639–9645
- [21] C. van Wüllen, *Z. Phys. Chem.* 224 (2010) 413–426
- [22] C. Adamo and V. Barone, *J. Chem. Phys.* 110 (1999) 6158–6170